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A general relationship for the compressibility of organic solvents

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Applying an additional hydrostatic pressure, which is determined by the difference ($B_i - B_j$) in Tait's equation coefficients, to liquids (S_j) with a higher compressibility coefficient equalizes the compressibility of all the liquids studied (S_i). The correlation obtained makes it possible to predict the compression curve of any liquid over a wide pressure range based on the value of β_T determined at ambient pressure.

The activation volumes ($\Delta V^{\neq}$) and reaction volumes ($\Delta_{r-n}V$) provide important information on a process mechanism and allow one to predict the effect of pressure on the reaction rate and equilibrium.[1–3] For isopolar processes, such as the Diels–Alder reaction, the changes in the solvent properties induced by pressure do not affect the rate and equilibrium constants and hence do not alter the ($\Delta V^{\neq}$) and ($\Delta_{r-n}V$) values determined. Reliable and consistent data on the effect of pressure on both forward and reverse processes have been obtained for this reaction.[4] The effect of solvent electrostriction can be very strong for polar and ionic processes, which often results in negative partial molar volumes of ions in solution.[5–8]

The compressibility of liquids ($\partial V/\partial P$) is the main reason of electrostriction.[1,2,6,8] Organic solvents differ greatly in physical and chemical properties and hence in solvation energy, which explains the large effect of the environment on the rate and equilibrium of polar and ionic processes.[9,10] The compressibility of a liquid depends on the balance of intermolecular attraction and repulsion forces. The liquid state involves intermolecular cavities, which provides the translational and rotational motion of molecules.[1,10] The volume decrease of a liquid ($\Delta V/V_0$) upon a moderate increase in pressure (up to ~3 kbar) results from the compression of these intermolecular cavities[1,10,11] and is reliably described by Tait's equation

$$\Delta V/V_0 = C\ln[(B + P)/B]. \quad (1)$$

Recent analysis of a large set of compressibility data ($N = 272$) revealed that the 'non-crossing rule' is observed for V–P curves.[12] It means that a distinct linear dependence (2) between the tangent modulus [$K_0 = 1/\beta_0 = -V_0(\partial P/\partial V)_T$] at atmospheric pressure and the secant modulus at 1000 bar ($-1000V_0/\Delta V_{1\ \mathrm{kbar}}$) is observed for compounds with quite diverse properties. This dependence is observed for compounds of various classes and over a wide temperature range.[12]

$$1/\beta_0 = (-4559 \pm 22.9) + (0.9865 \pm 0.0010)(1000V_0/\Delta V_{1\ \mathrm{kbar}}); \quad (2)$$
$$R = 0.9999;\ N = 272$$

A few unsuccessful attempts[6,12,13] to predict the compressibility of liquids have been undertaken based on other known molecular properties, such as molecular refraction, density, boiling point, viscosity, surface tension, packing factor, enthalpy of evaporation and vapour pressure. The compressibility is an independent parameter of a liquid, which is valuable for attaining a deeper understanding of the liquid behaviour.

Another interesting property of P–V curves is considered in this work. The compressibility of even a very thin liquid can be used as a basis for predicting the compressibility of very dissimilar liquids.

Gibson and Loeffler noted[13] that the compressibility of substituted benzenes can be predicted based on the compressibility of benzene, taking into account the difference in coefficients B. The values of C were considered as a measure of the intermolecular repulsion forces that are the same for benzene derivatives, while the values of B were correlated[13] with the difference in the intermolecular attraction forces. Gibson and Loeffler[13] interpreted the coefficient B as the resulting internal pressure equal to the difference between the Hildebrand cohesive pressure[14] determined by intermolecular attractive forces, on the one hand, and the expansive pressure resulting from the thermal motion energy, on the other hand. By now, ample data on the compressibility of liquids in a broad range of temperatures and pressures have been accumulated.[1,6,12] Analysis of these data shows that, given a proportional variation of the value of B, coefficient C in Tait's equation (1) for all the liquids studied previously[12] can be considered as a constant of 0.094. This results in compressibility curves that differ by no more than 2% from the experimental curves. As an example, Table 1 lists a few liquids from the database[12] that represent various classes of nonpolar, polar aprotic and protogenic solvents, whose compressibility coefficients differ more than fivefold.

Let us consider the compressibility curves of low-boiling liquids, namely, diethyl ether and *n*-hexane (Figure 1). The values of coefficient C for these liquids, like those for the rest of the solvents in Table 1, can be considered to be the same within ±2%. It follows from equation (1) that the compressibility curve of diethyl ether will almost coincide with that of *n*-hexane (*a*) at pressures above 98 bar ($B_2 - B_1$, Table 1). Similarly, it can be

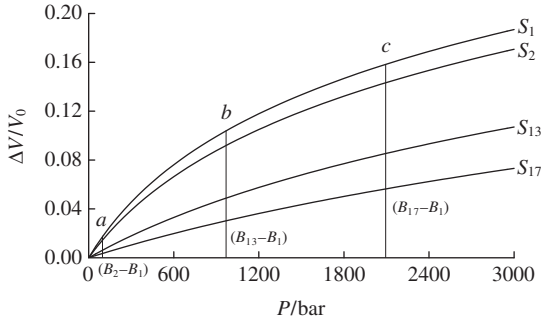

Figure 1 Compressibility curves of *n*-hexane (S_2), anisole (S_{13}), and ethane-1,2-diol (S_{17}) with new origins of coordinates *a*, *b* and *c*, respectively, coincide with the compressibility curve of diethyl ether (S_1).